

(12) UK Patent Application (19) GB (11) 2 294 330 (13) A

(43) Date of Printing by UK Office 24.04.1996

(21) Application No 9600481.7

(22) Date of Filing 09.07.1994

(30) Priority Data
(31) 4325157 (32) 27.07.1993 (33) DE
4342731 15.12.1993

(88) International Application Data
PCT/DE94/00791 De 09.07.1994

(87) International Publication Data
WO95/04273 De 09.02.1995

(71) Applicant(s)
Robert Bosch GmbH

(Incorporated in the Federal Republic of Germany)

Postfach 30 02 20, D-70442 Stuttgart 30,
Federal Republic of Germany

(72) Inventor(s)
Karl-Hermann Friese
Helmut Weyl

(51) INT CL⁶
G01N 27/407

(52) UK CL (Edition O)
G1N NBPT N25A1 N25C4D N25D2
U1S S1484

(56) Documents Cited by ISA
GB 2200460 A EP 0620528 A WO 92/08127 A
WO 88/08131 A DE 002619746 A DE 002504207 A
FR 002299643 A US 4626337 A US 4569748 A
US 4145272 A

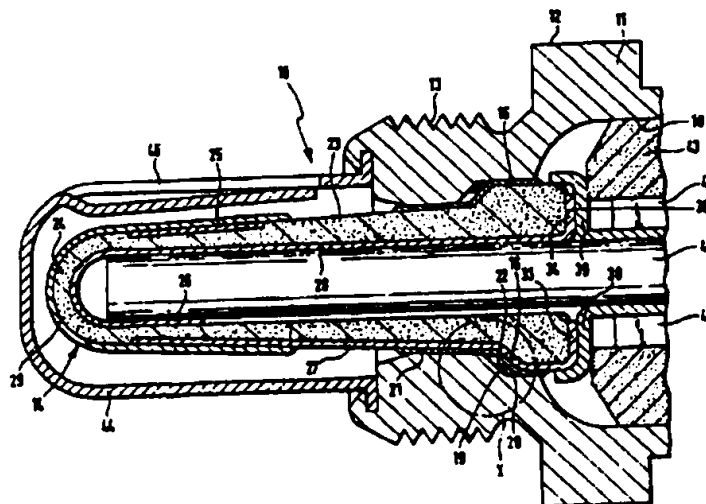
(58) Field of Search by ISA
INT CL⁶ G01N

(72) cont
Siegfried Nees
Hans-Martin Wiedenmann

(74) Agent and/or Address for Service
A A Thornton & Co
Northumberland House, 303-306 High Holborn,
LONDON, WC1V 7LE, United Kingdom

(54) Electrochemical measurement sensor with a potential-free sensor element and process for producing the same

(57) An electrochemical measurement sensor (10) for determining the oxygen content of gasses, in particular the oxygen content of exhaust gas from internal combustion engines, has a potential-free sensor element (14) with an oxygen ion-conductive solid electrolyte body (23) shaped as a pipe closed at one end. The solid electrolyte body (23) has on its outer surface an outer electrode (25) with a conductor strip (27) at the connection side which also extends on the outer surface, and is set into a metallic housing (11) with a sealing ring (20). The sensor element (14) has at least in the area of the sealing ring (20) an electrically insulating layer (21) which covers at least the conductor strip (27) towards the housing (11). The insulating layer (21) is made of a mixture of a crystalline, non-metallic material and of a vitrifying material. During manufacture, the insulating layer (21) is subjected to a thermal treatment at a temperature above the melting point of the vitrifying material, so that the insulating layer (21) forms a glaze filled with the crystalline, non-metallic material.



GB 2 294 330 A

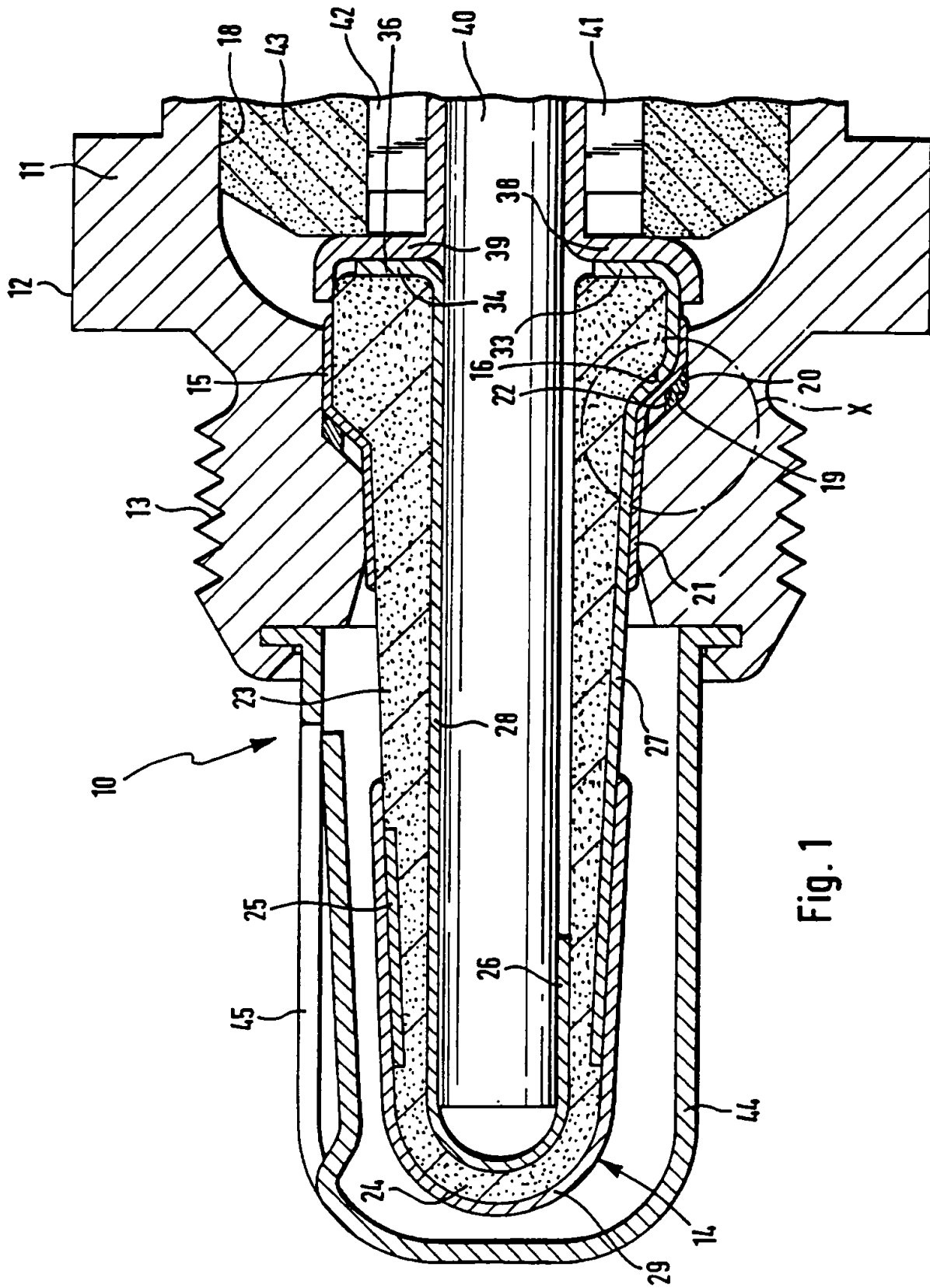
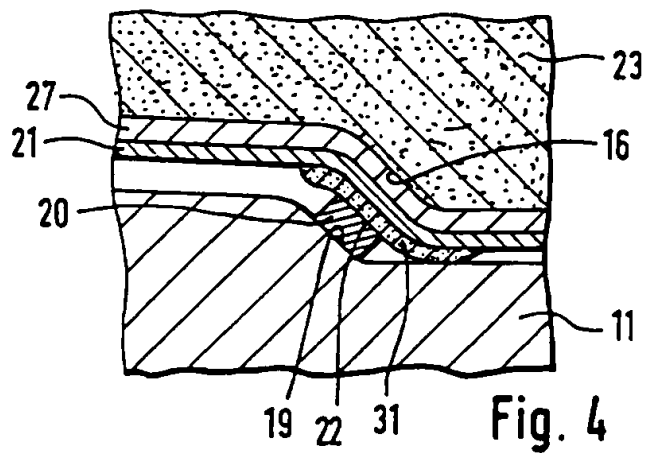
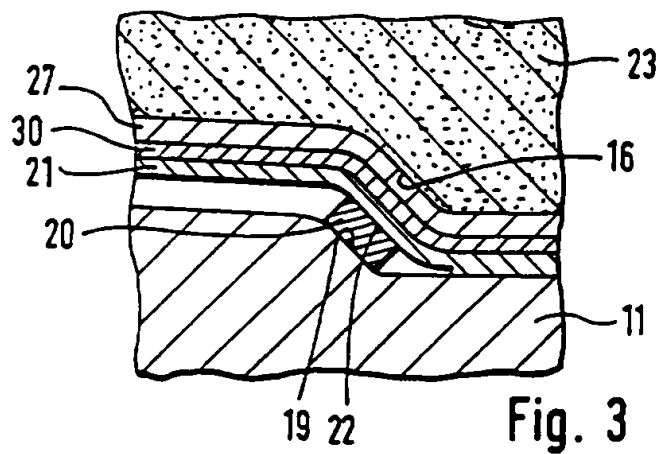
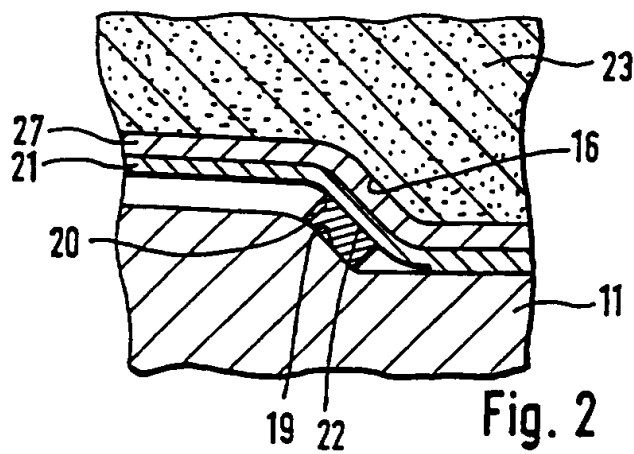


Fig. 1



Electrochemical measuring probe with a sensor element arranged in a floating manner, and process for its manufacture

Prior art

The invention is based on an electrochemical measuring probe according to the type of Claim 1. Electrochemical measuring probes are constructed, for example, in the so-called finger design, in which a solid electrolyte body in the form of a closed pipe is secured in a metal housing in a leak-tight manner. In the case of the finger probes a distinction is made between the floating and the non-floating measuring probes. In the non-floating measuring probes the track of the external electrode is contacted to the housing by means of an electrically conducting sealing ring. In the floating measuring probes, each electrode connection is fed directly to a control unit so that no electrical contacting with the housing is permitted. In both cases there must be a seal between solid electrolyte body and housing.

A floating measuring probe is known from DE-OS 25 04 206, in which several electrically insulating ceramic sealing rings of sintered alumina with $> 90\% \text{ Al}_2\text{O}_3$ are used, which create a hermetically sealed, electrically insulated connection between solid electrolyte body and the metallic housing. A seal of this kind is very complicated from the structural point of view, and also relatively risky because of the multiple parallel sealing with three sealing rings.

From DE-OS 26 19 746 it is also already known to cover the track on the solid electrolyte body with a glaze in order to avoid corrosive attacks, particularly in the regions of lower temperature.

Advantages of the invention

In contrast the measuring probe according to the invention with the characterizing features of Claim 1 has the advantage

that, in order to seal the sensor element in the housing, sealing elements can be used which are electrically conducting, such as a metal sealing ring or a graphite sealing ring and/or a graphite packet. The use of these compact seals prevents exhaust gas, water and/or fuel from being able to reach the inside of the sensor element. The insulating layer has high mechanical strength with respect to pressure peaks which arise because of the sealing ring in the assembly process. The process according to the invention has the advantage that it can be integrated into the production process of sensor elements. Proven techniques such as rolling, spraying of a suspension, flame-spraying, plasma-spraying, printing or the like can be used to apply the insulating layer.

Advantageous developments of and improvements to the measuring probe according to the invention and the process according to the invention are possible by means of the measures quoted in the sub-claims. A particularly good electrical insulation is achieved if the electrically insulating layer is formed from an oxide ceramic material and an alkaline earth silicate. A ceramically filled glaze is produced from the mixture with a subsequent heat treatment.

To prevent the glass-forming material from penetrating into the material of the electrically conducting connection it is appropriate to arrange an intermediate layer under the insulating layer, at least in the region of the electrically conducting connection, which intermediate layer preferably comprises the material of the solid electrolyte body. The materials of the insulating layer have a high insulation resistance at high usage temperatures compared to layers of solid electrolyte material. The raw materials used are inexpensive to obtain.

To prevent and/or reduce pressure peaks of a sealing element, such as a metallic sealing ring, on the insulating layer it is

also particularly advantageous to provide the insulating layer with a cover layer, at least in the region of the sealing ring. This prevents cracks from forming in the insulating layer, cracks which would otherwise have a negative effect on the insulating action and strength of the insulating layer. Furthermore the cover layer used acts as a diffusion barrier for disturbing cations, such as heavy metal cations like Cu^+ , Cu^{2+} , Fe^{2+} , which come from the sealing element (copper-coated steel sealing ring, for example) and can cause a certain electrical conductivity in the insulating layer and hence destroy the insulating effect, at least at high temperatures.

The process can be particularly efficiently integrated into the manufacturing process by co-sintering the insulating layer and/or the further applied layers together with the solid electrolyte body. Furthermore, the insulating layer has excellent adhesion, brought about in particular by the co-sintering. A thermal expansion of the insulating layer extensively matched to the material of the solid electrolyte body also has a positive effect on the layer adhesion. The impervious insulating layer also protects the solid electrolyte body from hydrothermal attacks, particularly in the low temperature range (150 to 300 °C). This improves the structural stability of the solid electrolyte body.

Drawing

Exemplary embodiments of the invention are shown in the drawing. Fig. 1 shows a longitudinal section through the part of a measuring probe on the exhaust gas side, and Figs. 2, 3 and 4 show exemplary embodiments of an enlarged sealing zone X according to Fig. 1.

Description of the exemplary embodiments

The electrochemical measuring probe 10 shown in Fig. 1 has a metallic housing 11 which, on its external side, has a hexagon

socket 12 and a thread 13 as fixing means for installation in a measuring gas pipe which is not shown. The housing 11 has a longitudinal bore 18 with a seal seat 19 which carries a sealing ring 20. A sensor element 14 with a shoulder 16 formed on a bead-shaped head 15 rests on the seal seat 19 provided with the sealing ring 20. A sealing surface 22 on the sensor element side is formed between sealing ring 20 and sensor element 14 on the bead-shaped head 15 of the sensor element 14. For its part the seal seat 19 forms a sealing surface on the housing side. The sealing zone X forming on the sealing ring 20 is shown enlarged in Figs. 2 to 4.

In this example the sensor element 14 is a per se known oxygen probe which is preferably used for measuring the oxygen partial pressure in exhaust gases. The sensor element 14 has a tubular solid electrolyte body 23, the end section of which on the measuring gas side is sealed by means of a base 24. On the external side exposed to the measuring gas, a layer-shaped gas-permeable measuring electrode 25 is arranged on the solid electrolyte body 23 and on the side facing the inner chamber, a gas-permeable and layer-shaped reference electrode 26 which is exposed to a reference gas such as air. The measuring electrode 25 is guided to a first electrode contact 33 with a measuring electrode track 27 and the reference electrode 26 to a second electrode contact 34 with a reference electrode track 28. The electrode contacts 33, 34 are each located on a front face 36 formed by the open end of the solid electrolyte body 23. A porous protective layer 29 is laid over the measuring electrode 25 and partially over the measuring electrode track 27. Advantageously the tracks 27, 28 are constructed as cermet layers and co-sintered.

The sensor element 14 projecting from the longitudinal bore 18 of the housing 11 on the measuring gas side is surrounded at a distance by a protective pipe 44, which has openings 45 for the measuring gas to enter and/or escape and which is secured at the end of the housing 11 on the measuring gas side. The

inner chamber of the sensor element 14 is filled, for example, by a rod-shaped heating element 40 which, and these details are not shown, is locked at a distance from the measuring gas and is provided with line connections.

A first contact part 38 rests on the first electrode contact 33 and a second contact part 39 on the second electrode contact 34. The contact parts 38, 39 are formed in such a way that they rest on the tubular heating element and are contacted with a measuring electrode connection 41 and a reference electrode connection 42. The connections 41, 42 are contacted with connecting cables which are not shown and are led to the outside to a measuring or control unit.

An insulating sleeve 43, which preferably comprises a ceramic material, is also incorporated in the longitudinal bore 18 of the housing 11. The insulating sleeve 43 is pressed onto the contact parts 38, 39 with the aid of a mechanical means which is not shown, and this creates the electrical connection to the electrode contacts 33 and 34.

To produce an electrically insulating and gas-tight fixing of the sensor element 14 in the housing 11, the shoulder 16 formed on the bead-shaped head 15 sits on the housing 11 by means of the sealing ring 20. To seal off the inner chamber of the sensor element 14, metal or graphite are suitable in particular as material for the sealing ring 20. Because of their high degree of compaction these materials are particularly impermeable to gas, water and fuel. A steel sealing ring with a 10 micrometre copper coating or a 20 micrometre nickel coating, for example, is appropriate.

A clearer illustration of the sealing zone X between the sensor element 23 and the housing 11 can be seen in Figs. 2 to 4. It is, however, essential to the use of an electrically conducting sealing ring 20 that the sensor element 14 is floating with respect to the metallic housing 11. For this

purpose, in a first exemplary embodiment according to Fig. 2 the track 27 is covered with an electrically insulating layer 21, particularly in the region of the sealing surface 22 on the sensor element side. The insulating layer 21 has a layer thickness of 20 to 100 micrometres. In this exemplary embodiment the insulating layer 21 is drawn over the entire region of the track 27 and round the circumference of the solid electrolyte body 23 which is adjacent to the housing 11. It is, however, equally conceivable to restrict the insulating layer 21 solely to the region of the sealing surface 22 and/or to extend the insulating layer 21 on the measuring gas side as far as the protective layer 29, which is advantageous because shunts as a result of carbon black and/or other conductive deposits from the exhaust gas can be avoided by this means, if the protective layer is sufficiently electrically insulating, such as plasma-sprayed Mg-spinel for example.

A further exemplary embodiment according to Fig. 3 comprises coating the tracks 27 with an intermediate layer 30, preferably of the material of the solid electrolyte body, and placing the insulating layer 21 according to the exemplary embodiment already described over the intermediate layer 30, wherein the intermediate layer 30 is also appropriately co-sintered. In this case the intermediate layer 30 has the function that the glass-forming material of the insulating layer 21 does not diffuse into the material of the track 27 and thus influence the conductivity of the track 27.

The material of the insulating layer 21 is selected in such a way that it withstands the pressure forces of the sealing ring 20 which arise when the sensor element 14 is assembled in the housing 11, and that it also tolerates usage temperatures in the region of the joining point at least up to 700 °C. This is achieved in that a crystalline non-metallic material in homogenous distribution forms a bearing support framework in a glaze layer and the transformation temperature of the glass phase lies above the usage temperature.

Advantageously the specific electrical resistance of the crystalline non-metallic material has at least 10 times the value of the specific electrical resistance of the solid electrolyte body. Materials which can be considered are : Al_2O_3 , Mg-spinel, forsterite, MgO-stabilized ZrO_2 , CaO- and/or Y_2O_3 -stabilized ZrO_2 , with low stabilizer contents, advantageously with a maximum of 2/3 of the stabilizer oxide of the full stabilization, non-stabilized ZrO_2 or HfO_2 , or a mixture of these substances.

An alkaline earth silicate, such as Ba-Al-silicate, is used as the glass-forming material. The Ba-Al-silicate has a coefficient of thermal expansion of $\approx 8.5 \times 10^{-6} \text{ K}^{-1}$ for example. The barium can be replaced by strontium up to 30 atom %.

The alkaline earth silicate can be incorporated as pre-melted glass frit or as glass phase raw material mixture, wherein the latter is advantageously freed from water of crystallization, carbonate or other loss on ignition to a large extent in a calcination process. A small amount ($< 10 \text{ wt.}\%$) of a glass-forming raw material mixture is advantageously added to the glass frit. The material mixture may contain electrically conducting impurities only up to a maximum of 1 wt.%. This relates in particular to Na_2O , K_2O , Fe_2O_3 , TiO_2 , Cu_2O or similar semi-conducting oxides. The content of electrically conducting impurities is preferably under 0.2 wt.%.

A third exemplary embodiment is shown in Fig. 4, in which a cover layer 31 is arranged over the electrically insulating layer 21 in the region of the sealing surface 22 on the sensor element side, so that the sealing ring 20 rests on the cover layer 31 on the sensor element side. The layers which adjoin each other on the sensor element side correspond to the exemplary embodiment of Fig. 1. It is, however, equally conceivable for the layers on the sensor element side to be produced according to the exemplary embodiment of Fig. 3. The cover layer 31 is an impervious ceramic layer which preferably

(comprises) the material of the solid electrolyte body 23, yttrium-stabilized ZrO_2 , for example. To produce an impervious layer the flux content of the ceramic starting material is selected to be less than 10 per cent, wherein no addition of flux produces the most impervious layer. The cover layer 31 itself must have no insulation resistance, but rather it can have an appreciable electron and/or ion conductivity. In the case of an electrical conductivity the cover layer 31 may not overlap the insulating layer 21. The layer thickness of the cover layer 31 is appropriately between 10 and 50 micrometres. It has also proved advantageous to match the coefficient of thermal expansion of the cover layer 31 to the coefficient of thermal expansion of the solid electrolyte to within approx. $\pm 2 \times 10^{-6} \text{ K}^{-1}$.

Different examples of the composition and manufacture of the insulating layer 21 and the cover layer 31 are described below:

Example 1:

Composition of the inorganic raw material mixture:

60 wt.% of alumina (99.5 wt.% of Al_2O_3 , < 0.1 wt.% of Na_2O),
specific surface $15 \text{ m}^2/\text{g}$

40 wt.% of Ba-Al-silicate glass powder (53 wt.% of BaO , 5 wt.% of Al_2O_3 , 42 wt.% of SiO_2 , specific surface $5 \text{ m}^2/\text{g}$).

The raw materials are ground and homogenized for two hours in a ball mill with 90% Al_2O_3 grinding balls. An aqueous slip is then prepared with 500 g of raw material mixture of alumina and Ba-Al-silicate glass, 500 ml of distilled water and 25 ml of 10% aqueous polyvinylalcohol solution. The slip is ground in a ball mill with 90% Al_2O_3 grinding balls for a grinding time of 1.5 hours.

The slip is brush-applied to the solid electrolyte body 23 comprising partially stabilized ZrO_2 (5 mol% of Y_2O_3) and pre-sintered at 1000°C , in the region of the insulating layer 21

according to Fig. 1. The slip is then co-sintered together with the solid electrolyte body 23 for approx. three hours at 1450 to 1500 °C so that the insulating layer according to Fig. 1 forms. To assemble the measuring probe the sensor element 14 is placed on the sealing ring 20. At a sealing ring temperature of 500 °C, in this embodiment the insulation resistance is over 300 kOhm. By way of comparison the insulation resistance of a sensor element 14 that was provided only with a coating of a ZrO_2 partially stabilized with 5 mol% of Y_2O_3 in the region of the sealing zone 22 is under 5 kOhm at 500 °C sealing ring temperature.

Example 2:

The difference between this example and the raw material mixture of Example 1 is that the following composition is chosen instead of the 40 wt.% of Ba-Al-silicate glass powder:
 38 wt.% of Ba-Al-silicate glass powder,
 1 wt.% of kaolin,
 1 wt.% of barium carbonate (BaCO_3 , chemically pure),
 insulation resistance > 300 kOhm.

Example 3:

The composition of the raw material mixture differs from Example 1 in that the following constituents are used instead of the Ba-Al-silicate glass powder:
 40 wt.% of a calcinate comprising:
 11 wt.% of kaolin,
 34 wt.% of quartz (99% SiO_2) and
 55 wt.% of BaCO_3 (chemically pure).

The constituents are ground in a ball mill with 90% Al_2O_3 grinding balls for two hours and calcined for two hours as loose material in alumina capsules in oxidizing atmosphere at 1000 °C and then ground again as described. Insulation resistance > 300 kOhm.

Example 4:

The composition of the raw material mixture differs from Examples 1 and 3 as follows:

70 wt.% of alumina and 30 wt.% of calcinate,
insulation resistance > 300 kOhm.

Example 5:

As example 4, but with the following instead of the alumina:
70 wt.% of partially stabilized ZrO_2 with 3.5 wt.% of MgO (35% monoclinic), specific surface $7 \text{ m}^2/\text{g}$,
insulation resistance > 20 kOhm.

Example 6:

As Example 3, but with:
50 wt.% of alumina,
50 wt.% of calcinate,
insulation resistance > 300 kOhm.

Example 7:

As Example 3, but with:
85 wt.% of alumina,
15 wt.% of calcinate,
insulation resistance > 200 kOhm.

Example 8:

The composition of the raw material mixture corresponds to Example 6. In this case, however, the slip is sprayed with a glazing gun onto the solid electrolyte body which has been sintered to complete imperviousness at 1450 to 1500 °C. The insulating layer is then sintered in for two hours at 1300 to 1350 °C in oxidizing atmosphere.
Insulation resistance > 100 kOhm.

Example 9:

The composition corresponds to Example 7, wherein the alumina contains the following constituents:
99.3% of Al_2O_3 , 0.3% of Na_2O ,

specific surface $2.5 \text{ m}^2/\text{g}$,
insulation resistance $> 100 \text{ k}\Omega$.

Example 10:

The composition corresponds to Example 6, but with the following constituents instead of the alumina:

50 wt.% of monoclinic zirconium oxide powder with no stabilizer added ($99.5\% \text{ ZrO}_2 + \text{HfO}_2$)

specific surface $8.5 \text{ m}^2/\text{g}$,
insulation resistance $> 100 \text{ k}\Omega$.

Example 11:

The composition corresponds to Example 3, but with the following constituents instead of the alumina:

60 wt.% of Mg-spinel powder (MgOAl_2O_3) with $< 0.5 \text{ wt.}\%$ of free MgO and $< 0.1 \text{ wt.}\%$ of Na_2O ,

specific surface $8 \text{ m}^2/\text{g}$,
insulation resistance $> 300 \text{ k}\Omega$.

Example 12:

The insulating layer 21 is applied to the solid electrolyte body 23 as described in Example 1. The insulating layer 21 is dried for approximately an hour in the air-circulating oven at 120°C for example. The cover layer 31 of part-stabilized zirconium oxide with 5 mol% of Y_2O_3 is then applied. Printing pastes or spray suspensions which are per se known in the prior art are used to produce the cover layer 31, wherein the cover layer 31 is brush-applied in this example. Finally the solid electrolyte body 23 is co-sintered for three hours at 1450° to 1500°C with the electrodes and the electrode tracks, the insulating layer 21 and the cover layer 31.

Example 13:

The insulating layer 21 is produced as in Example 12, but instead of the drying process the solid electrolyte body 23 and the insulating layer 21 are pre-sintered at approx.

1000 °C. The cover layer 31 is then applied and co-sintering carried out according to Example 12.

Example 14:

Manufacture is according to Example 13, but in this case the insulating layer 21 comprises 50 parts by weight of alumina and 50 parts by weight of Ba-Al-silicate powder.

Example 15:

The insulating layer 21 comprises the material according to Example 1. Co-sintering takes place after the insulating layer 21 has been applied. The cover layer 31 of forsterite powder is then applied by means of a flame spraying process. Two hours' tempering at 1300 °C then takes place.

Example 16:

The insulating layer 21 is produced according to Example 15. In this case the cover layer 31 comprises magnesian spinel and is applied in the plasma spraying process without subsequent tempering. The layer thickness of the cover layer 31 is appropriately selected at 10 micrometres in this case.

Example 17:

The composition of the raw material mixture of the insulating layer 21 corresponds to Example 6 in this case. The slip is sprayed onto the solid electrolyte body 23 which has been completely sintered at 1450 ° to 1500 °C by means of a glazing gun according to Example 8. The insulating layer 21 is then sintered in for two hours at 1300 °C in oxidizing atmosphere. The cover layer 31 is then produced according to Example 16.

Claims

1. Electrochemical measuring probe for determining the oxygen content of gases, particularly for determining the oxygen content in exhaust gases of internal combustion engines, with a sensor element arranged in a floating manner, which sensor element has an oxygen ion conducting solid electrolyte body, preferably in the form of a pipe closed on one side, and electrodes with electrically conducting connections, wherein the sensor element is inserted into a metallic housing with a sealing ring and at least one electrically conducting connection facing the housing is electrically insulated with respect to the housing by means of an electrically insulating layer in the region of the sealing ring, characterized in that the insulating layer (21) is formed of a mixture of a crystalline non-metallic material and a glass-forming material in such a way that a glaze filled with the crystalline non-metallic material forms on heating.
2. Measuring probe according to Claim 1, characterized in that one of the two materials in each case makes up at least 10 vol.% of the mixture.
3. Measuring probe according to Claim 1, characterized in that the crystalline non-metallic material comprises Al_2O_3 , Mg-spinel, forsterite, MgO-stabilized ZrO_2 , CaO- and/or Y_2O_3 -stabilized ZrO_2 , non-stabilized ZrO_2 or HfO_2 or a mixture of these substances.
4. Measuring probe according to Claim 1, characterized in that the insulating layer (21) has a coefficient of thermal expansion which is at least approximately matched to the coefficient of thermal expansion of the material of the solid electrolyte body (23).

5. Measuring probe according to Claim 4, characterized in that the crystalline non-conducting material has a coefficient of thermal expansion of $> 6 \times 10^{-6} \text{ K}^{-1}$, preferably $> 7 \times 10^{-6} \text{ K}^{-1}$.

6. Measuring probe according to Claim 1, characterized in that the glass-forming material is an alkaline earth silicate glass.

7. Measuring probe according to Claim 6, characterized in that the alkaline earth silicate glass is a barium aluminium silicate glass.

8. Measuring probe according to Claim 7, characterized in that up to 30 atom% of barium are replaced by strontium.

9. Measuring probe according to Claim 1, characterized in that an intermediate layer (30) is arranged between the electrically conducting connection (27) and the insulating layer (21) at least in the region of the electrically insulating section (27).

10. Measuring probe according to Claim 9, characterized in that the intermediate layer (30) comprises the material of the solid electrolyte body (23).

11. Measuring probe according to Claim 1, characterized in that the electrically insulating layer (21) is placed round the solid electrolyte body (23) at least in the region of the sealing ring (20).

12. Measuring probe according to Claim 1, characterized in that the insulating layer (21) reaches as far as a protective layer (29) covering the measuring electrode (25).

13. Measuring probe according to Claim 1, characterized in that the layer thickness of the insulating layer (21) is 10 to 100 micrometres.

14. Measuring probe according to Claim 1, characterized in that a cover layer (31), which is capable of absorbing mechanical pressure forces of the sealing ring (20), is placed over the insulating layer (21) at least in the region of the sealing ring (20).

15. Measuring probe according to Claim 14, characterized in that the cover layer (31) is an impervious ceramic layer to whose material a flux of less than 10% is added prior to the sintering.

16. Measuring probe according to Claim 15, characterized in that the material of the cover layer (31) comprises the material of the solid electrolyte body (23).

17. Measuring probe according to Claim 14, characterized in that the thickness of the cover layer (31) is 10 to 50 micrometres.

18. Process for manufacturing a sensor element arranged in a floating manner for a measuring probe according to Claim 1, characterized in that the mixture of the insulating layer comprising the crystalline non-conducting material and the glass-forming material is subjected to a heat treatment above the melting temperature of the glass-forming material.

19. Process according to Claim 18, characterized in that the glass-forming material is incorporated into the mixture as pre-melted glass frit.

20. Process according to Claim 19, characterized in that the glass frit is used with an addition of a glass-forming raw material mixture < 10%.

21. Process according to Claim 18, characterized in that the glass-forming material is incorporated into the mixture as a mixture of glass-forming raw materials.

22. Process according to Claim 18, characterized in that the glass-forming raw materials are freed from water of crystallization, carbonate or similar losses on ignition in a calcination process, to an extent $> 90\%$.

23. Process according to Claim 18, characterized in that the heat treatment of the insulating layer (29) takes place by co-sintering with the solid electrolyte body (23).

INTERNATIONAL SEARCH REPORT

Intern. Application No.

PCT/DE 94/00791

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N27/407

According to International Patent Classification (IPC) or to both national classification and IPC:

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 626 337 (Y. HOTTA) 2 December 1986 see column 3, line 54 - column 5, line 22 ---	1
A	US,A,4 569 748 (M. YAMAKAWA) 11 February 1986 see column 4, line 23 - column 5, line 15 ---	1
A	EP,A,0 520 528 (GENERAL MOTORS CORPORATION) 30 December 1992 see page 4, column 44 - page 5, column 49 ---	1
A	WO,A,88 08131 (ALLIED CORPORATION) 20 October 1988 see page 7, line 7 - page 8, line 20 ---	1
A	US,A,4 145 272 (K. NAKAMURA) 20 March 1979 see column 4, line 33 - line 53 ---	1
	--- -/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *B* earlier document but published on or after the international filing date
- *I* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

20 September 1994

Date of mailing of the international search report

19. 10. 94

Name and mailing address of the ISA

European Patent Office, P.O. 5818 PatentAan 2
NL - 2280 HV Rijswijk
Tel.: (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

CALLEWAERT, H

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/DE 94/00791

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 08127 (R. BOSCH) 14 May 1992 see claim 1 ---	1
A	FR,A,2 299 643 (R. BOSCH) 27 August 1976 cited in the application see claims ---	1
A	DE,A,26 19 746 (R. BOSCH) 24 November 1977 cited in the application see claim 1 ---	1
A	DE,A,25 04 207 (R. BOSCH) 5 August 1976 ---	
A	GB,A,2 200 460 (HITACHI) 3 August 1988 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No.

PCT/DE 94/00791

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4626337	02-12-86	NONE	
US-A-4569748	11-02-86	NONE	
EP-A-0520528	30-12-92	JP-A- 5188034	27-07-93
WO-A-8808131	20-10-88	US-A- 4750256	14-06-88
		AU-A- 1362088	04-11-88
		EP-A- 0356434	07-03-90
US-A-4145272	20-03-79	NONE	
WO-A-9208127	14-05-92	DE-A- 4034072	30-04-92
		DE-A- 4126378	30-04-92
		EP-A- 0506897	07-10-92
		US-A- 5246562	21-09-93
FR-A-2299643	27-08-76	DE-A- 2504206	05-08-76
		JP-C- 1184694	20-01-84
		JP-A- 51103494	13-09-76
		JP-B- 58016144	29-03-83
		SE-B- 428331	20-06-83
		SE-A- 7600941	02-08-76
		US-A- 4019974	26-04-77
DE-A-2619746	24-11-77	NONE	
DE-A-2504207	05-08-76	NONE	
GB-A-2200460	03-08-88	JP-A- 63171356	15-07-88
		FR-A- 2609550	15-07-88